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Robust Microporous Metal-Organic Frameworks for Highly Efficient and Simultaneous Removal of Propyne and Propadiene from Propylene

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Abstract: Simultaneous removal of trace amount of propyne and propadiene from propylene is an important but challenging industrial process. In this study, we reported a class of microporous metal-organic frameworks (**NKMOF-1-M**) with exceptional water stability and remarkably high uptakes for both propyne and propadiene at low pressures. Attributed to the strong bind affinity to propyne and propadiene over propylene, **NKMOF-1-M** created new benchmark selectivities for ternary propyne/propadiene/propylene (0.5/0.5/99.0) mixture, and set as a unique MOF platform to achieve both the highest selectivity and productivity of polymer-grade propylene (99.996%) at ambient temperature, verified by both simulated and experimental breakthrough results. Moreover, we demonstrated a rare example to visualize propyne and propadiene molecules in the single-crystal structure of **NKMOF-1-M** through a convenient approach under ambient condition, which helped to precisely understand the binding sites and affinity of propyne and propadiene. These results provide important guidance on using ultramicroporous MOFs as physisorbent materials to resolve industrial challenges related to ternary propyne/propadiene/propylene mixture separation.

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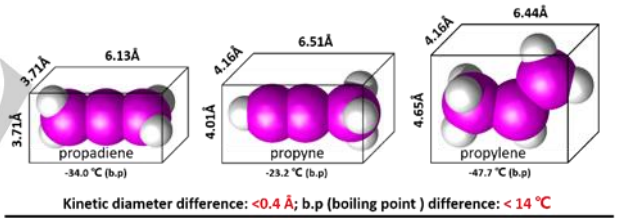
Propylene (C_3H_6) is an important olefin raw material in petrochemical industry that is widely used as essential building blocks for the production of polypropylene, propylene oxide and acrylonitrile. The worldwide production capacity of propylene had reached 120 million tons in 2017, second only to the production of ethylene.[1] The production of propylene, mainly derived from the cracking of naphtha or the fractional distillation of hydrocarbon, inevitably introduces a trace amount of propyne and propadiene as impurities, which will severely poison the catalysts used in propylene polymerization.[2] To increase the lifetime and efficiency of those expensive catalysts, impurity (propyne+propadiene) content must be reduced to 40 ppm or less in propylene polymerization.[3] Currently, the dominated technique to remove trace amount of propyne and propadiene is selective hydrogenation using noble metal catalysts, which usually suffers from some disadvantages including high cost, short lifetime, low efficiency and possible secondary pollution.[4] Therefore, developing new approaches for efficient and simultaneous removal of trace amount of propyne and propadiene is of great significance and urgently needed.



Scheme 1. Molecular structure and physical property of propyne, propadiene and propylene (b. p = boiling point).

Separation strategies based on physical adsorption are attracting widespread attention due to their environmentally friendly and energy efficiency. However, using traditional porous materials such as zeolites[5,6] and activated carbon[7] to separate ternary propyne/propadiene/propylene gas mixture has not been realized yet. It could be ascribed to the similar physical properties, close structures and molecular sizes of propyne, propadiene and propylene (Scheme 1).[8] In the past two decades, metal-organic frameworks (MOFs) have emerged as a new class of porous materials and demonstrated great potentials to overcome the limits of conventional porous materials (e.g. structure monotonous, lack of specific binding sites), ascribed to their well-defined structure, fine-tunable pore size and custom-designed functional groups.[9-13] Many efforts have been devoted to use MOFs for binary gas mixture separation, such as acetylene/ethylene,[14-19] ethylene/ethane,[14,20-22] carbon dioxide/methane,[23,24] carbon dioxide/nitrogen,[25,26] acetylene/carbon dioxide,[27,28] krypton/xenon,[29]

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propyne/propylene[30,31] and propylene/propane.[32] However, simultaneous removal of propyne and propadiene from propylene using MOFs as absorbents is still underexplored.[8] Exploring new MOF adsorbents to simultaneously remove propyne and propadiene from propylene is of great importance to industrial production of highly pure propylene.

(Cu[M(pdt)$_2$], pdt = pyrazine-2,3-dithiol, M = Cu, Ni) materials were prepared via previously reported procedures.[19] **NKMOF-1-M** exhibits a three-dimensional (3D) framework constructed by four-connected [M(pdt)$_2$]$^-$ building blocks (Figure 1). **NKMOF-1-M** possess one-dimensional (1D) square channels with a pore size around 5.7 Å (after subtracting van der Waals radius) along the *c* direction. Interestingly, both conjugated pyrazines and metal centers (Cu or Ni) locating on the wall of the 1D channels can provide two distinct binding sites (Figure 1) to gas molecules, that are potential to benefit the gas capture or separation application.[19]

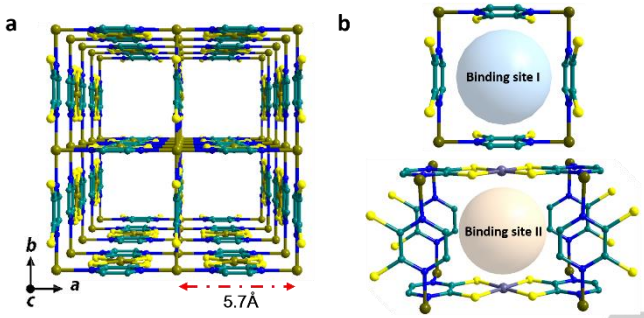

Figure 1. (a) The 3D structure of **NKMOF-1-M** with 1D channels along the *c* axis; (b) The two distinct binding sites in **MKMOF-1-M**. Atom colors: C = teal, N = blue, S = yellow, Cu = turquoise, Ni = blue gray.

Notably, **NKMOF-1-M** (M = Ni or Cu) can still retain their porosity and crystallinity after soaking in water for more than one year at room temperament, as verified by Powder X-ray diffractometer (PXRD) and BET surface area measurements (Figure S1-S3). N_2 sorption isotherms collected at 77 K revealed that **NKMOF-1-Ni** and **-Cu** possessed close BET surface areas (374 m^2/g and 382 m^2/g, respectively) and almost identical pore sizes (~5.4 Å) (Figure 2a). To explore the potential of **NKMOF-1-Ni** and **-Cu** for simultaneous ternary (propyne, propadiene and propylene) gas mixture separation, single-component gas adsorption data of propyne, propadiene and propylene were collected at different temperatures (273K, 298K, 308K and 318K) (Figure 2b and Figure S4). We found that **NKMOF-1-Ni** and **-Cu** can adsorb 3.5 mmol/g and 3.3 mmol/g of propyne and 3.3 mmol/g, 3.0 mmol/g of propadiene at 1.0 bar and 298 K, which are much higher than the uptake of propylene (2.1 mmol/g and 1.8 mmol/g, respectively). Noteworthily, the propyne and propadiene adsorption of the two adsorbents exhibited steep curves in the low-pressure region at all tested temperatures (273 K, 298 K, 308 K and 318 K), indicative of their strong binding affinity to propyne and propadiene. Gas adsorption selectivity is usually closely related to the adsorption behavior in the low-pressure region. Thus, we closely examined the adsorption behaviors for each gas in low-pressure region at 298 K (Figure 2c and Figure S5). Notably, **NKMOF-1-M** can achieve remarkably high uptakes for both propadiene and propyne at ultra-low pressure region. For instance, at pressure <1 mbar, propadiene uptake capacity of **NKMOF-1-Ni** and **-Cu** created new records (1.43 mmol/g and 1.30 mmol/g, respectively, at 1 mbar) which surpassed current benchmark adsorbents (Figure S5b).[8] And at pressure <0.1 mbar, **NKMOF-1-M** also possessed the highest propyne capacity (1.21 mmol/g and 1.10 mmol/g for **NKMOF-1-Ni** and **-Cu**, respectively, at 0.1 mbar). Meanwhile, the uptake capacity of propylene is relatively low (< 0.08 mmol/g) for **NKMOF-1-Ni** and **-Cu** at <1 mbar. This remarkable propyne and propadiene adsorption behavior in the ultra-low-pressure region indicated remarkably strong gas-sorbent interactions and high selectivity over propylene for **NKMOF-1-M**.

The isosteric enthalpy of adsorption (Q_{st}) can quantitatively represent the binding affinity of sorbents towards gases. Thus, the adsorption isotherms of single-component gas were fitted with the Dual-Site-Langmuir-Freundlich (DSLF) isotherm model (Table S1-S6). The Q_{st} of propyne was then calculated based on the DSLF method[34,35] (Table S7-S11), which afforded the results of 65.1 kJ/mol and 67.2 kJ/mol for **NKMOF-1-Ni** and **-Cu**, respectively, at zero coverage (Figure S6). Although the obtained Q_{st} curve shapes are uncommon due to difficulties to extract reasonable Q_{st} values from empirical fitting (see Supporting Information for explanation), the zero-coverage Q_{st} values for both MOFs are close to the corresponding adsorption energies that were calculated for propyne about the primary binding site through density functional theory (DFT) as explained later. The same calculation methods afforded Q_{st} of propadiene (54.0 kJ/mol and 45.2 kJ/mol) and propylene (38.0 kJ/mol and 37.2 kJ/mol) for **NKMOF-1-Ni** and **-Cu** (Figure S7 and S8). These results manifest that **NKMOF-1-M** possess much stronger binding affinity to propyne and propadiene than propylene. Overall, due to the remarkably high uptakes and strong binding affinity for propyne and propadiene, **NKMOF-1-M** possessed great potential to simultaneously remove trace propyne and propadiene from propylene.

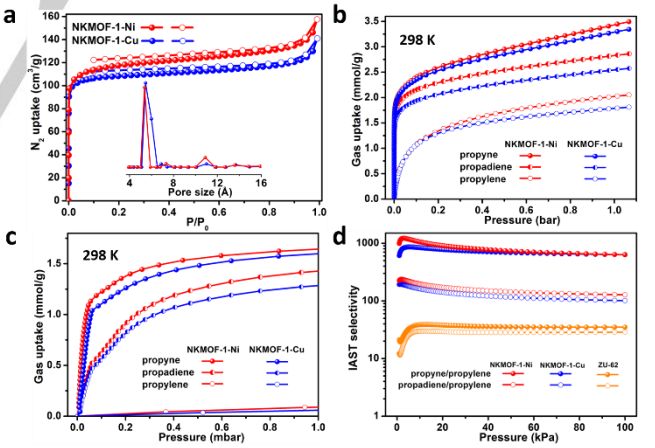

Figure 2. (a) N_2 adsorption isotherms at 77 K and pore size distributions of **NKMOF-1-M**; (b) Propyne, propadiene and propylene adsorption isotherms at 1 bar and 298 K; (c) Propyne, propadiene and propylene adsorption isotherms at 1 mbar and 298 K; (d) IAST selectivities of ternary mixture (propyne/propadiene/propylene=0.5/0.5/99 (v/v/v)) for **NKMOF-1-M** compared with current benchmark material (**ZU-62**) at 298 K.

In order to evaluate the separation performance of adsorbent materials, we calculated ternary gas mixture (propadiene/propyne/propylene = 0.5/0.5/99, v/v/v) selectivity using ideal adsorption solution theory (IAST). As displayed in Figure 2d and Table S12, the propadiene/propylene and

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propyne/propylene selectivity of **NKMOF-1-Ni** were ranging from 127.5 to 236.5, and 630.4 to 1217.8, respectively, at 1-100 kPa. The selectivities of **NKMOF-1-Cu** were slightly lower than those of **NKMOF-1-Ni**, ranging from 100.8 to 193.4 for propadiene/propylene and 610.5 to 859.5 for propyne/propylene. Notably, the selectivity of both **NKMOF-1-Ni** and **NKMOF-1-Cu** are more than a magnitude better than that of the benchmark material **ZU-62** (11.5-30.0 for propadiene/propylene and 21.3-38.9 for propyne/propylene at 1-100 kPa) (Figure 2d). Thus, **NKMOF-1-Ni** and **-Cu** offer new benchmark selectivities with respect to propadiene/propyne/propylene separation.

To gain deep insight into binding sites of propyne and propadiene in the **NKMOF-1-M** platform, we obtained the crystal structure of **NKMOF-1-Cu** capturing propyne (**propyne@NKMOF-1-Cu**) and propadiene (**propadiene@NKMOF-1-Cu**), in which we can precisely study the binding sites between gas molecules and the framework of **NKMOF-1-M** and verify the results of the simulation study. Activated **NKMOF-1-Cu** crystals suitable for single-crystal X-ray diffraction (SCXRD) were placed in corresponding gas atmosphere at room temperature with propyne or propadiene balloons, respectively. SCXRD data was then collected at 120 K controlled by the liquid nitrogen purge. Interestingly, structural solution shows that propyne and propadiene molecules with full site occupancy were located between the four pyrazine rings (Figure 3), consistent with the strong binding site I (Figure 1b, S9a and S9c), determined by modelling study. Additionally, we found propyne molecule formed strong hydrogen bonds (HC≡C–CH_3···S, HC≡C–CH_3···C) with the two sulfur atoms and one carbon atom of pyrazine ring (H···S, H···C distances is 3.02 Å, 2.95 Å and 2.88 Å, respectively). Propadiene molecule also formed strong hydrogen bonds (H_2C=C=CH_2···S, H_2C=C=CH_2···C) with the two sulfur atoms and one carbon atom of pyrazine ring (H···S distances is 3.17 Å, 3.13 Å and 3.19 Å, respectively). Propyne and propadiene molecules do not appear at the other weaker binding site (II). This result confirms that propyne and propadiene preferentially bind to site I at ambient condition.

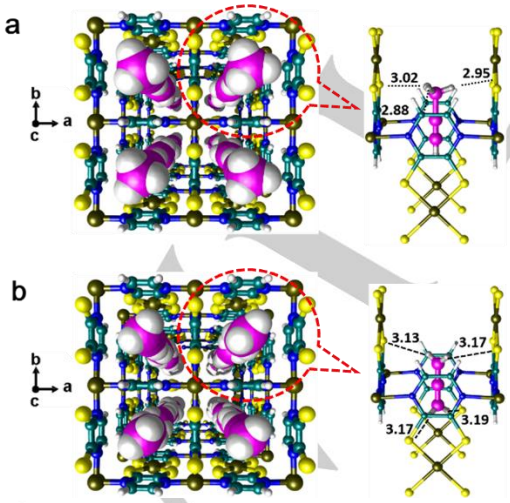

Figure 3. (a) Single crystal structure of **propyne@NKMOF-1-Cu** with propyne molecules orderly located in the 1D channels; (b) Single crystal structure of **propadiene@NKMOF-1-Cu** with propadiene molecules orderly located in the 1D channels. Atom colors: C(MOF) = teal, C(propyne and propadiene) = pink, H = white, N = blue, S = yellow, Cu = gold.

Periodic DFT calculations were performed to evaluate the propyne, propadiene and propylene adsorption sites and energies in **NKMOF-1-M**. The DFT calculations revealed that both adsorbate molecules, propyne and propadiene, prefer to localize about two sites: (I) between four neighboring pyrazine units, and (II) between the open-metal sites of two adjacent MS_4 units (Figure S9 and S10). The region between the pyrazine units is a highly favorable binding site for the propyne and propadiene molecules in both MOFs. As the propyne and propadiene molecule is adsorbed here, π–π interactions between the adsorbate molecule and the surrounding pyrazine units are expected, along with H···S hydrogen bonding interactions with the nearby S atoms. For propyne in **NKMOF-1-Cu**, the three H···S (HC≡C–CH_3···S) bonding distances are 2.77, 2.77, and 2.85 Å (Figure S9a). For propadiene, the four H···S (H_2C=C=CH_2···S) bonding distances are 3.02, 2.96, 2.92, and 2.87 Å in **NKMOF-1-Cu** (Figure S9c). Such H···S distances for both adsorbates are in reasonable agreement with those observed in the MOF through single crystal X-ray diffraction (Figure 3). The corresponding distances in **NKMOF-1-Ni** are somewhat shorter than those obtained for **NKMOF-1-Cu**, which indicates that **NKMOF-1-Ni** exhibits greater interactions with the propyne and propadiene molecules at this site. Comparison of the H···S bonding distances for propyne and propadiene at site I for both MOFs revealed that such distances for propyne are all shorter than those of propadiene, which manifests that propyne molecules have stronger host-guest interactions with **NKMOF-1-M** and is consistent with the results of the single component adsorption isotherms (Figure 2c). The calculated adsorption energies for propyne at site I in **NKMOF-1-Ni** and **NKMOF-1-Cu** are -72.3, -71.3 kJ mol^{-1}, respectively, while those for propadiene at the same site are -68.1 kJ mol^{-1}, -64.5 kJ mol^{-1}, respectively (Table S13 and S14). At site II in both MOFs, a favorable interaction exists between the negatively charged C atoms of the alkyne moiety and the positively charged metal ions of the MS_4 units (Figure S9 and S10). Hydrogen bonding interactions also occur between the H atoms of the adsorbate and the nearby S atoms of the framework at this site. Adsorption energies of -47.2 and -51.1 kJ mol^{-1} were calculated for propyne about site II in **NKMOF-1-Ni** and **-Cu**, respectively, while adsorption energies of -43.7 kJ mol^{-1}, -48.2 kJ mol^{-1} were calculated for propadiene about the same site in the respective MOFs (Table S13 and S14). GCMC simulations indicate that saturation of propyne and propadiene in **NKMOF-1-M** was achieved at 2.5 molecules per unit cell (Figure S11-S14). The experimental saturated adsorption data for propyne and propadiene of **NKMOF-1-Ni** (~2.3 molecules per unit cell to propyne; 2.2 molecules per unit cell to propadiene at 1 bar, Figure S14 and S15) agreed well with the simulated result. The adsorption of propylene about site I in the two MOFs is less energetically favorable than that for propyne and propadiene at this site, with calculated adsorption energies of -59.0 and -57.0 kJ mol–1 for NKMOF-1-Ni and -Cu, respectively (Table S13 and S14).

Transient breakthrough simulations were performed to evaluate the polymer-grade propylene (propyne+propadiene < 40 ppm) productivities of tested MOFs for the separation of ternary mixture (propyne/propadiene/propylene = 0.5/0.5/99) at industrial conditions. Figure S20 reveals the outlet concentrations of propyne+propadiene exiting the fixed bed with these MOFs materials as a function of the dimensionless time,τ, at 1 bar and 298 K. when the outlet concentration of propyne+propadiene is

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less 40 ppm, the results consistent with IAST selectivity, the τ break value for **NKMOF-1-Ni** and **-Cu** are much longer than the other benchmark materials. For the hierarchy of τ break value, **NKMOF-1-Ni** > **NKMOF-1-Cu** > **ZU-62**. Moreover, **NKMOF-1-Ni** and **NKMOF-1-Cu** possess the first and second highest propylene productivities up to 191.1 mol/L and 163.3 mol/L, respectively (Figure S20b and Table S12). Noteworthily, the separation performance of adsorbents in the industrial fixed-bed adsorber are evaluated via not only gas mixture selectivity, but also productivity of desired gases. Thus, **NKMOF-1-M** demonstrated excellent propyne/propadiene/propylene separation performance which surpass current benchmark materials, and set as a unique MOF platform to achieve both high selectivity and propylene productivity.

In order to establish the feasibility of ternary mixture (propyne/propadiene/propylene) separation on tested MOFs under kinetic conditions, breakthrough experiments were performed, which are strongly pertinent to the vacuum swing adsorption (VSA) process, an energetically efficient method for industrial-scale separations. Breakthrough experiments were measured on an in-house-constructed separation apparatus[1] (Scheme S1), in which propyne/propadiene/propylene (0.5/0.5/99) mixtures were used as feeds to mimic the industrial process conditions. As we expected from the single-component adsorption isotherms, **NKMOF-1-Ni** displayed the best propyne/propadiene/propylene (0.5/0.5/99) mixture separation abilities at 298 K. In Figure 4a, propylene was firstly eluted through the bed, while propyne and propadiene were still adsorbed, affording the pure polymer-grade propylene with non-detectable propyne and propadiene, whereas the **NKMOF-1-Ni** retained propylene for a remarkable time before the breakthrough of propadiene and propyne. After a certain period of time, propadiene and propyne were eluted from the column and quickly reached equilibrium. The retained time of pure propylene (propyne+propadiene < 40 ppm) for propyne/propadiene/propylene (0.5/0.5/99) mixture on **NKMOF-1-Ni** reached to 1825 min/g, more than 1.5 times higher than the benchmark MOFs material, **ZU-62** (701 min/g). Notably, the performance of **NKMOF-1-Ni** is also much better than commercial Zeolite 5A (3 min/g) and Zeolite 4A (0 min/g). The hierarchy of retained time is **NKMOF-1-Ni** > **NKMOF-1-Cu** > **ZU-62** > **Zeolite 5A** > **Zeolite 4A** under the same condition (Figure 4 and Figure S21). Moreover, such excellent propyne/propadiene/propylene (0.5/0.5/99) breakthrough performance on **NKMOF-1-M** was closely associated with its ultrahigh propyne/propylene and propadiene/propylene IAST selectivity at room temperature. The productivity of pure propylene (propyne+propadiene < 40 ppm) captured from the mixture in **NKMOF-1-Ni** and **-Cu** was up to 230 mol/L and 216 mol/L, which created new benchmarks (Figure 4c and Table S15).

To investigate the reusability and structural stability on **NKMOF-1-M** (M = Ni or Cu), cycling breakthrough experiments for propyne/propadiene/propylene (0.5/0.5/99) mixtures associated PXRD measurement were tested on **NKMOF-1-Ni** under the same conditions as described above. Due to the inconvenient activation condition, **NKMOF-1-Cu** was not studied here. The breakthrough curves for ternary mixture (propyne/propadiene/propylene=0.5/0.5/99) in five cycles are almost overlapped (Figure 4d), and the crystallinity of **NKMOF-1-Ni** retained (Figure S1), indicative of the excellent regenerability and stability of **NKMOF-1-Ni**.

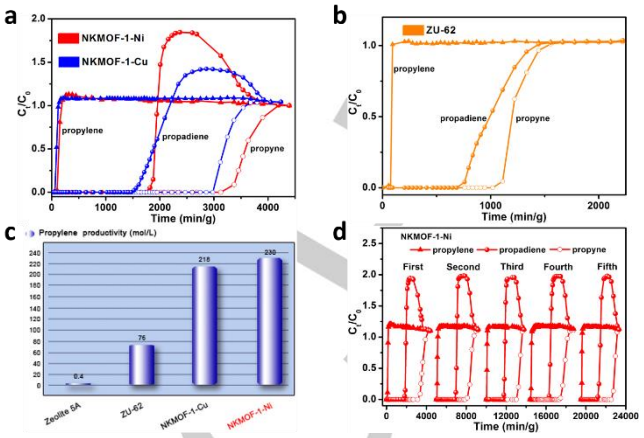

Figure 4. (a) Propyne/propadiene/propylene (0.5/0.5/99) mixture breakthrough curves of **NKMOF-1-Ni** (red) and **NKMOF-1-Cu** (blue); (b) breakthrough curves of previous benchmark material, **ZU-62** (orange); (c) propylene productivity of benchmarking materials; (d) Breakthrough cycling test of **NKMOF-1-Ni**; Gas: propylene = tringle, propadiene = solid circle, propyne = empty circle.

In summary, we developed a class of robust microporous MOFs (**NKMOF-1-M**, M = Cu or Ni) with strong binding affinity for both propyne and propadiene. **NKMOF-1-M** displayed remarkably high uptakes for both propyne and propadiene: the highest yet observed at ultra-low pressure and room temperature. These results made **NKMOF-1-M** the best MOF adsorbents to separate propyne and propadiene from propylene. The selectivities of **NKMOF-1-Ni** and **-Cu** are more than a magnitude better than that of the benchmark material, **ZU-62**. Both of the simulated and experimental ternary gas mixture breakthrough results confirmed the best propyne/propadiene/propylene separation performance of **NKMOF-1-M**. This work provides important guidance on designing adsorbent materials with strong binding affinity to propyne and propadiene via tailoring pore aperture and introducing strong gas-sorbent interactions such as hydrogen bonding interactions and π–π interactions. This study also paves a new avenue for the design of adsorbent materials for simultaneous removal of multi-component gases mixtures.

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Keywords: Metal-organic frameworks, ternary gas separation, propylene purification, binding site, computation

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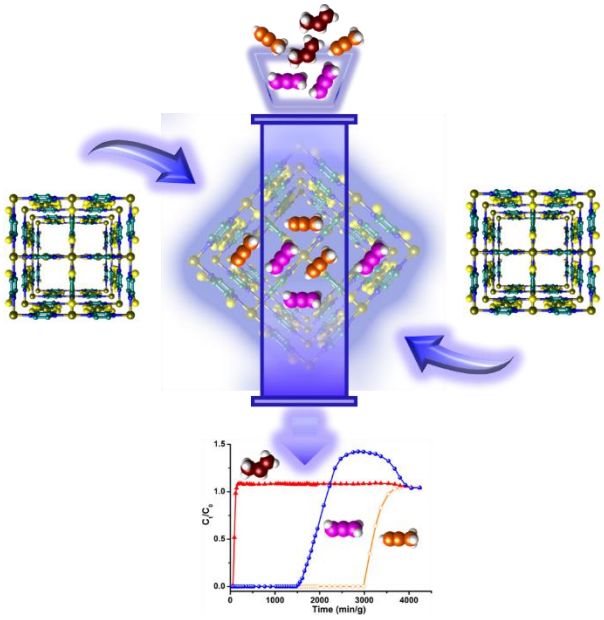

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